Synthetic gas bench study of a natural gas vehicle commercial catalyst in monolithic form: On the effect of gas composition

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ABSTRACT

With growing concerns about global environmental and increased focus on population health is renewed interest in transportation sector. The challenge is to find and develop cost effective ways to improve urban air quality without scarifying economy. The natural gas, as fuel, constitutes an alternative to the traditional fuels because its impact on the reduction of the global warming impact is consequent compared to the traditional fuels such as gasoline. This study deals with a study of NGV's catalysts. Natural gas vehicles' catalysts were characterized by XPS, STEM in order to determine the various active phases. The results of characterization showed that the palladium oxidized Pd^{2+} was the principal active site. The experimental runs were carried out close to the real operating conditions using a sample of monolith. Numerous reactions were identified, such as NO reduction by hydrogen, carbon monoxide at low temperature and methane at high temperature. Moreover, methane reforming and water-gas shift were clearly found on commercial system. The influence of each reaction on the kinetics behaviour of the whole mixture makes difficult to uncouple the different reactions of oxidations and reductions, because the rate of these reactions was highly dependant on the reactant present in the automobile exhaust gases as well as their relative concentration. To identify each involved reaction in NGV TWC process, we remove alternatively reducing agents or oxidizing agents.

1. Introduction

Nowadays there are 4.7 million of natural gas vehicles in operation all around the world. Recognised as the cleanest hydrocarbon fuel, compressed natural gas generates a reduction in 24% of CO_2 emissions if compared with a gasoline vehicle and 80% of nitrogen oxides if compared with diesel vehicles. As matter of fact, natural gas vehicles (NGV) programs are currently developing very rapidly in Europe and especially in France for public transportation. CNG engines can operate under lean conditions so that the fuel efficiency can be much increased compared to stoichiometric conditions. Under these conditions, unburned methane, a potent greenhouse gas, is emitted in the exhaust gases [1].

In Europe, since the year 2000, the Euro standard defines a limit value, for methane emissions from heavy-duty NGVs, equal to 1.6 g kW^{-1} during a transient ETC cycle. In order to meet the future severe regulations [2], in stoichiometric or in lean conditions, a catalytic exhaust converter is necessarily installed on NGVs sold for the European Market. Thus, the major issue is to develop an efficient post-treatment capable to treat simultaneously the NO$_x$, CO and mainly the excess of unburned methane present in the exhaust gas.

Thus, in stoichiometric conditions, three-way catalysis (TWC), initially used for exhaust gas treatment of gasoline vehicles, is the most efficient solution for post-treatment of NGV exhaust gas. However, in an economic point of view, these catalysts are more expensive for a GNV application due to their higher content in noble metals to oxidize efficiently the unburned methane. The use of three-way catalytic converters to minimise air pollution caused by automotive exhaust gases is already well established [3,4] for vehicles fuelled by gasoline. However, only few studies dealt with the use of catalysts used in simulated exhaust gases from CNG vehicles [5–7].

The TW catalysts contain noble metals (Pt, Pd, Rh) deposited together with a washcoat (alumina modified with small amounts of lanthanum or barium and with ca. 10–20% ceria and zirconia) on a ceramic or metallic monolith [4]. Provided the air/fuel (A/F) ratio is controlled within a narrow operating window, both the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides is promoted [8,9].

Thus the reduction of NO and the oxidation of CO and hydrocarbons are the major reactions of TWC process. However,

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exhaust gases do not only contain hydrocarbons, carbon monoxide and nitrogen oxides: large amounts of steam and carbon dioxide are also present. Thus, all these gases can have an important role in the catalytic performance [10–17].

As already mentioned by Whittington et al. [18,19], the reactions occurring over the catalyst could include total and partial oxidation of hydrocarbons, oxidation of hydrogen, water-gas shift, steam reforming and CO_2 reforming of hydrocarbons. Of these, CO_2 reforming is too slow to compete with steam reforming [20]. Both steam reforming and water-gas shift are known to be promoted by three-way catalysts [10–20]. The relative importance of oxidation, steam reforming and water-gas shift over different catalysts has been the subject of few studies [14,15,18]. The role of ceria, known to be a promoter for the water-gas shift reaction [14,18,21] and steam reforming [12,15,18,22] has also been studied. However, few systematic studies of the separate and the combined reactions over directly comparable catalysts have been attempted. Only Whittington et al. [18,19] tried to separate all these contributions.

The present paper reports a study of a commercial three-way catalyst dedicated to natural gas compressed (NGC) vehicle. The honeycomb catalyst was used in synthetic gas bench with a simulated exhaust gas. In order to evidence the importance of each gas, the reaction mixture was modified in keeping always the same air/fuel ratio ($\lambda = 0.995$). Thus, we try to show that NO was reduced mainly by hydrogen at low temperature and methane at high temperature, whereas CO is only oxidized by molecular oxygen. At high temperatures water-gas shift (WGS) and methane steam reforming act as important reactions.

2. Experimental

2.1. Catalysts samples

The catalyst is a commercial three-way converter dedicated to NGV. It has been extracted from a French compact car. After the cordierite monolith extraction, samples "carrots" were prepared (diameter: 1 in., length: 1.9 in.). The monolith is composed of 600 channels per square inches (CPSI). Before runs and characterization, the carrots were calcined in industrial air at 500 °C for 2 h, using a heating rate of 3 °C min^{-1}.

2.2. Characterization of catalysts

The commercial catalysts, before and after reaction, were characterized by elementary analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM), by X-ray photoelectrons spectroscopy (XPS). The specific surface area was also measured using a home made apparatus. Main physico-chemical properties of the catalysts (washcoat) are reported in Table 1. The balance is made by Silica, traces of Barium and Lanthanum and traces of support (Mg).

Elementary analysis was performed by the "Service Central d'Analyses du CNRS" in order to determine the noble metal

contents (Rh, Pt, Pd). Powder X-ray diffraction was carried out on a Siemens model D-500 diffractometer with CuKα radiation. TEM was carried out on a microscope JEOL JSM-5510LV (low vacuum) coupled with a EDS (energy dispersion spectroscopy) system in order to determine the metallic particles on supports and to check their dispersion.

STEM was also performed on this commercial catalyst which is composed by cordierite used as support ($Al_3Mg_2AlSi_5O_{18}$) impregnated by the washcoat. The commercial catalyst was cut to obtain a carrot with a length of 1 cm. This carrot was metallized with gold in order to obtain a conducting surface by the means of a cathodic type plasma deposition.

XPS was performed in order to determine the oxidation state of the metal on the surface of the catalysts. XPS analysis was performed using a Vacuum Generators Escalab 220XL spectrometer. Measurements were performed under ultra-high-vacuum with a residual pressure of approximately 10^{-10} Torr. A monochromatized aluminium source was used for excitation. Charge effects were compensated by applying a flood gun source (6–8 V). The Al 2p binding energy value of 74.6 eV was used as internal reference. Simulation of the photopeaks was achieved using the Gaussian–Lorentzian mixture peak-fit software provided by VG Scientific. Subsequent quantification accounted for a non linear Shirley background substraction. In Table 2, we present the results obtained by XPS.

2.3. Catalytic activity studies

Each study was performed in temperature programmed surface reaction (TPSR). The heating rate was chosen equal to 10 °C min^{-1}. The TPSR were used to determine light off temperature of each pollutant present in the exhaust gases [4–16].

To be close to industrial conditions, our apparatus is composed by a pre-heater in which the gases are heated up to 790 °C. These heated gases flowed through the catalytic bed composed by the carrot of the monolith. Three thermocouples are available to follow the reaction temperature. One is place prior the catalyst, the second one close to the catalyst and the third at the exit of the reactor (at 10 cm from the catalyst). The temperatures given in this study are those obtained close to the catalyst. The gas hourly space velocity (GHSV) was chosen equal to 40,000 h^{-1}. The GHSV was calculated as follows:

$$GHSV(h^{-1}) = \frac{\text{Total gas flow } (cm^3\,h^{-1})}{\text{Volume of catalyst } (cm^3)} \quad (1)$$

We first investigated the influence of composition close to the stoechiometry. Thus, we change the gases composition in conserving a ratio air/fuel constant corresponding to $\lambda = 0.995$ which corresponds to a richness of 1.005. The experimental

Table 1
NGV converter composition.

	Catalyst composition (%)	
	1st run (ppm)	2nd run (ppm)
Pt	723	701
Rh	0.18	0.17
Pd	2.55	2.57
Ce	2.15	2.13
Al	23.98	23.42

Table 2
ESCA of the catalyst.

	XPS analysis	
Peak	Binding energy center	Atomic %
Ce 3d	883.3	0.84
Ba 3d	780.6	0.62
O 1s	531.3	46.44
Pd 3d$_{3/2}$	342.0	0.60
Pd 3d$_{5/2}$	336.7	0.64
Rh 3d	309.1	0.19
C 1s	285.0	20.74
Zr 3d	182.0	2.44
Al 2p	74.5	27.90

Table 3
Exhaust gases composition during the runs on the NGV converter, effect of NO concentration.

	Composition A	Composition B	Composition C	Composition D
NO (ppm)	2500	1640	1500	2000
CH_4 (ppm)	1700	1230	1400	1550
O_2 (ppm)	4800	4100	4800	4800
CO (ppm)	4700	3300	4700	4700
H_2 (ppm)	3400	2400	3400	3400
CO_2 (%)	9.25	9.43	9.25	9.25
H_2O (%)	18	18	18	18

conditions are presented in Table 3. We also studied the influence of the concentration of each gas in keeping the A/F ratio constant.

The NO mixture was supplied by Air Liquide as 10% NO, and 90% N_2 (<10 ppm other gases). The O_2 mixture contained 40% O_2, and 60% N_2 (Air Liquide). The CH_4 mixture contained 25% CH_4, and 75% N_2 (Air Liquide). The CO_2 mixture contained 100% CO_2 (Air Liquide). The CO mixture contained 79.5% CO and 20.5% N_2 (Air Liquide). The H_2 mixture contained 100% (Air Liquide). The water was injected in the feed in vapour form in using a liquid pump (Gilson) through a vapourisator placed at 120 °C. The total gas flow was maintained at 15.6 L min^{-1} NTP in order to maintain the desired GHSV. Each of the gas mixtures was metered using calibrated electronic mass flow controllers (Brooks, Model 5850R).

The reactor outflow was analyzed using a set of specific detectors. An Eco Physics NO_x Chemiluminescence's analyzer (for NO and total NO_x (i.e. NO + NO$_2$)) allowed the simultaneous detection of NO, NO$_2$ and NO$_x$. The chosen range was 0–2500 ppm. An IR analyzer was used to monitor N_2O and methane (0–2500 ppm). The CO is monitored by two specific IR analyzer dedicated to low (0–2000 ppm) and high CO concentrations (1–5%). Finally, the CO_2 is monitored by a Rosemount analytical detector (0–20%).

3. Results and discussion

3.1. What are the active phases of commercial natural gas TWC

In order to determine what the active phases responsible for pollutant abatement are, different characterizations were performed. Elementary analyses led to the conclusion that three metals are available to perform such reactions. The palladium (2.55%) is the major active phase of the commercial catalyst. Rhodium (0.18%) is also present. Finally a low amount of platinum (0.07%) was also detected. The supports are alumina and mixed phases of ceria zirconia. Platinum is also present but the amount was very low. These results are representative of typical TWC for gasoline vehicles (Table 1) [23]. No changes were observed after catalytic runs. For NGV applications, the methane which is the major component of natural gas (about 85%) is the main pollutant (green house effect). It is well known [24] that palladium species especially PdO possess the highest catalytic activity at relatively low temperature [24]. Thus, it is not surprising to find an active catalyst containing such large amount of palladium. Moreover, rhodium is well known for its properties in NO_x reduction. Thus, it is also not surprising to find Rhodium on the commercial converter [18].

By XRD, we try to identify the crystallized phases, however, due to the low amounts of metals nor rhodium or palladium were clearly identified.

Scan electronic microscopy was realized on the catalytic converter. This converter is a honeycomb typical TW catalyst. The surface of the material is not polished. The EDS measurements

were very difficult to carry out because a plane surface is needed in order to catch the secondary electrons (Fig. 1a). SEM was also performed in order to establish in what support the metals were deposit.

Two zones are well identified: the first one with aluminum and a second with cerium and zirconium. One can note (Fig. 1b) that palladium is supported on alumina. A detailed analyse showed that rhodium is present in the same zone in which appear cerium and zirconium. From SEM, we can conclude that two phases are present Pd/Al$_2$O$_3$ and Rh/CeZrO$_2$. The platinum was not detected due to the low amounts present on the catalyst. Again, no evolution is observed after runs.

This study was completed by a study in HRTEM coupled with EDS. By this technique, particles of Palladium supported on Al$_2$O$_3$ were found (Fig. 2). After distribution particle size calculation, it was found that the average size of PdO particles is 2 nm. Other crystallized domains with ceria–zirconia were found (10–20 nm) (Fig. 2). However, no particle of rhodium was detected. By EDS, we could conclude that the palladium is always present when alumina is present which is in agreement with SEM observations. More over, in other zones, by EDS, we clearly identified cerium and zirconium. No platinum was observed.

These techniques led us to propose that two main phases are present on the catalyst. The first one is a palladium phase, in which palladium could be in a metallic or cationic oxidation state (Pd^0 or Pd^{x+}); the second one is the rhodium (Rh^0 or Rh^{x+}). In TW catalysts, the active sites are still remaining to be debated [23,25].

In order to determine the oxidation state of the palladium and rhodium, XPS analyses were performed. Thus, ESCA (electron spectroscopy for chemical analysis) was used to characterize the first layers of the active phases [26]. The results are presented in Table 2. Thus, the main elements present on NGV converter were identified by this technique. Noble metals (Pd and Rh) and the supports (Al, O and Ce) were clearly identified. No platinum was detected by XPS. Finally, barium was also identified. In order to calculate the binding energies, the internal reference was chosen as the peak of Al 2p at 74.5 eV. The experimental deviation was ±0.2 eV. In accumulating spectra, the photopeaks of each element were obtained. The maximum of O 1s binding energy was found at 531.6 eV. The catalyst contains zirconium and palladium. Interferences exist between these two elements. The binding energy of Zr $3p_{1/2-3/2}$ was at 332.5 eV and those of palladium at 336.3 eV [27]. After a plot decomposition (figure not shown), we can conclude that the peak of Zr 3p corresponds to zirconium in ZrO$_2$ structure. Furthermore, this structure is confirmed by a peak at 182.3 eV corresponding to the binding energy of Zr 3d. The percentage of Zr at the surface is around 2.44% (Table 2).

The maximum of palladium peak was found at 336.6 eV. This value corresponds to Pd^{2+} probably stabilized in a PdO form [26]. Only, 0.6% of palladium is present at the surface, whereas palladium is the major noble metal present on the commercial converter. The palladium in PdO form is presented as the more active phase for methane oxidation [24,27,28]. However, we are not able to confirm that all palladium available at the surface is PdO. Indeed, Pd^{2+} surrounded by oxygen can exist at the surface of the catalyst.

By XPS, we notice also that barium is present on the catalyst. This metal is generally used in NO_x trap materials [29]. Kobayashi et al. [29] reported that barium had a positive effect on the stability of alumina supported palladium-based catalysts dedicated to NGV applications. Other authors proposed that BaO phase, as basic oxide, could stabilise the palladium in Pd^{2+} or PdO phases by electronic donor effects which can confer to palladium the catalytic properties of rhodium in terms of NO_x reduction. The photopeak of barium corresponds on our catalyst at oxidized barium in BaO form [30].
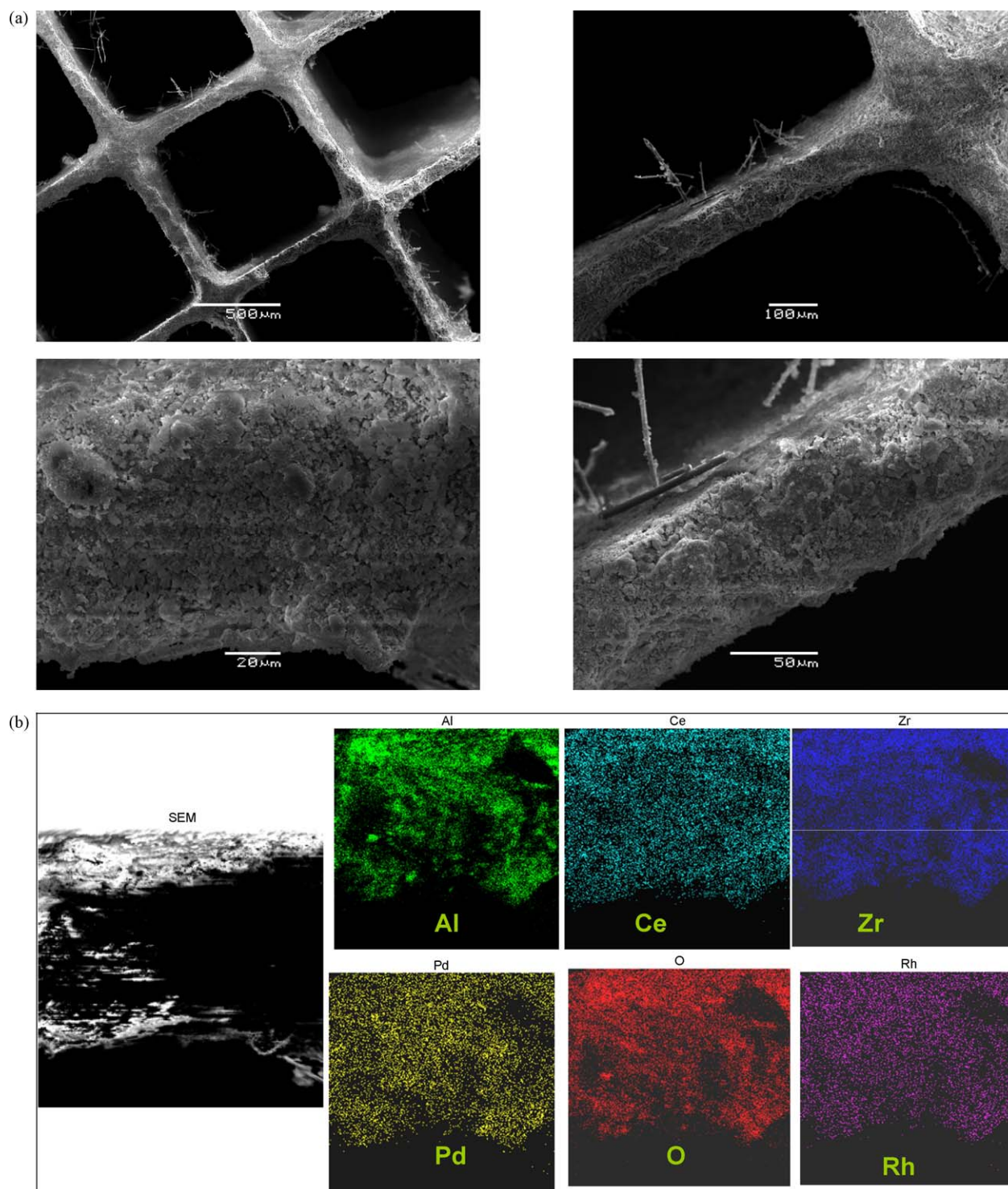
Fig. 1. SEM cartography of fresh NGV converter. (a) General view of the catalyst. (b) EDS cartography.

Cerium was also detected on the commercial catalyst. From STEM and TEM, we know that cerium and zirconium are in fact a mixed solid state solution corresponding ceria–zirconia. It is well known that ceria–zirconia leads to a higher durability and metal stabilisation of metals on commercial catalysts [31]. Moreover, ceria–zirconia plays also a role of OSC [32]. The obtained data let us to conclude that 33.6% of cerium is Ce^{3+} and 66.4% is Ce^{4+}, i.e. CeO_2, Ce_2O_3 or sub oxides as well described by Trovarelli [33]. Finally,

XPS spectra show that 0.18% of rhodium was at the surface. The binding energies at 309.2 and 314.2 eV correspond to rhodium Rh_2O_3 (308.8 eV). Thus, as palladium, the rhodium is present in the surface in a cationic form. No Pd^0 and Rh^0 were found on the catalysts. The results of XPS and Elementary analysis can be explained by the multi-layer catalysis of TW-catalysts or by an enrichment of Rh at the surface as already detailed in the literature [34]
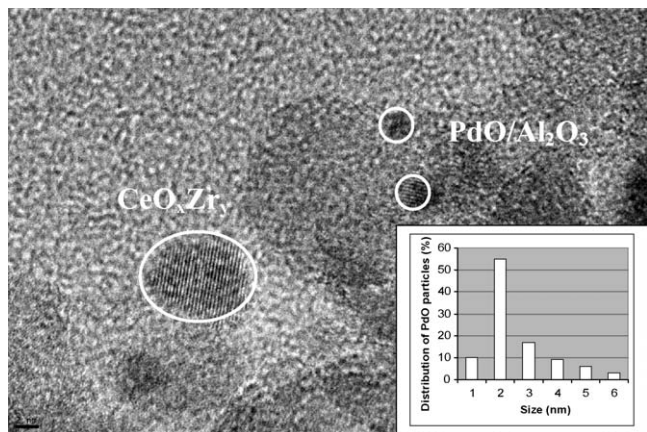
Fig. 2. HRTEM micrograph of NGV converter. Distribution of PdO particles on commercial catalyst.

3.2. What are the major reactions occurring during the natural gas TWC process

3.2.1. CO/NO/O$_2$/H$_2$ reactions

During the last years, the various reactions occurring between CO, NO and O$_2$ over three-way metallic catalysts were the subject of numerous studies [32–36]. As yet, active sites for these reactions are not well defined. Authors generally believe that zero-valent metal is responsible for the catalytic activity [35,38] as is the case for CO/O$_2$ and CO/NO reactions over rhodium catalysts. When the metallic phase is dispersed on a reducible support (CeO$_x$), CO can oxidize at lower temperatures by reacting with oxygen ions at the metal–support interface [37,39,40,41]. According to Cho [42], the N$_2$O desorption at low temperature is correlated with the beginning of the CO/NO reaction which can only start with the accessibility of the active sites initially occupied by N$_2$O. N$_2$O can also come to the dissociation of NO, at low temperature, two NO molecules dissocate and lead to N$_2$O, whereas at high temperature, the reaction of NO dissociation leads to N$_2$ formation [43]. N$_2$O formation was also observed over Pt/Al$_2$O$_3$ and Pt-CeO$_2$/Al$_2$O$_3$ catalysts, especially in the case of highly dispersed metallic phase [44]. Let us also note, that rhodium sites generating (NO)$_2$ species do not exclusively consist of zero-valent rhodium atoms, since dinitrosyl complexes can be evidenced on exchangeable rhodium ions in zeolites [45]. As for CO/O$_2$ reaction, reduced ceria can significantly improve the catalytic activity of the system in the CO/NO reaction [46,47], by the presence of oxygen vacancies at the metal support interface favouring the NO reduction; oxygen atoms originating from the dissociation of NO at the interfacial sites could locate in the oxygen vacancies, while retaining a labile character which makes possible an additional contribution to the CO oxidation.

In the presence of the three reagents (CO, NO, O$_2$), the two preceding reactions are competing, due to the fact that NO and O$_2$ compete for the active sites of the samples for the CO/NO/O$_2$ reactions. Leclercq et al. [37] have observed for Pt/Al$_2$O$_3$ low NO conversion as long as O$_2$ is present in the reagent mixture and have concluded that the NO adsorption sites could be blocked by adsorbed oxygen. Cerium oxide additive, here again, confers to the catalysts some promoting effect on their activity in the CO/NO/O$_2$ reactions, by generating at the metal–support interface additional bifunctional sites [38,14]; under an oxygen-deficient atmosphere, CO can migrate at the metal support interface to be oxidized by a ceria lattice oxygen with concomitant oxygen vacancy formation. From the above bibliography data, it appears that the CO/NO/O$_2$ reactions are complex and result from the competition between the CO/O$_2$ and CO/NO reactions. The active sites are not well defined yet, but it is generally admitted that the reaction takes place both on the reduced metal and at the metal support interface. High thermal stability and enhanced reducibility for the ceria-containing support are essential requirements. There still has been some controversy regarding the oxidation state of rhodium, some authors assuming this precious metal to be oxidized during the catalytic cycle [43,48]. Hyde et al. [48] considered individual rhodium atom sites or edge sites with cationic character due to some interactions between metal atoms and the support. Chuang and co-workers [49] on Rh/SiO$_2$, starting from Rh^0, considered that the reduction of NO by CO goes through the oxidation of Rh^0 to Rh$^+$ at the surface of the precious metal: then Rh$^+$ can chemisorb NO. Fajardie et al. [50] found CeO$_2$–ZrO$_2$ able to stabilize 100% rhodium as Rh^{x+} (with x probably equal to 1) into Ce^{4+} vacancies of the support. Thus, based on the literature, we can draw two simplified catalytic cycles for oxidation and reduction reactions involved in TWC process for natural gas applications, (*) represents on site (Fig. 3). The oxygen adsorbs at the surface and dissociates into O*. The NO can also dissociate or form dinitrosyl species prior reduction. Again, atomic oxygen O* is left on the active sites. These later sites are then regenerated by reducing agents such as hydrogen, carbon monoxide and methane. Salin et al. [51] have studied NO adsorption/desorption on commercial but simplified three-way catalysts (Pt alone, Pd alone or Rh alone on CeO$_2$–ZrO$_2$–Al$_2$O$_3$ honeycomb materials); this author has found that a fraction of NO adsorbed at room temperature always desorbed at the temperature of the reaction CO/NO/O$_2$ (for stoichiometric mixture), clearly evidencing that a fraction of the precious metal should be in an oxidized state. Furthermore, this result shows that it is always very difficult to completely reduce supported precious metals, probably due to very strong metal–support interactions. This result can also explain data from literature assuming the existence of oxidized transition metal atoms on materials globally considered as reduced catalysts [52]. On our commercial catalyst, the rhodium and the palladium are Rh^{3+} and Pd^{2+} respectively.
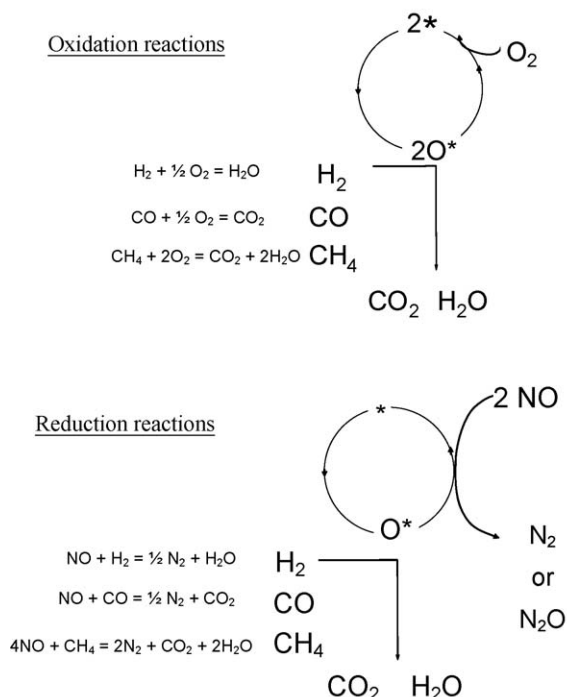

Fig. 3. Scheme of reactions involved in TWC process in presence of methane.

3.2.2. $CH_4/NO/O_2$ reactions

In comparison with typical TWC process, the reactions involved with natural gas are similar. However, one more reducing agent is present: the methane. Subramanian et al. [53] already studied the methane elimination from NGV in different conditions, lean burn, rich and stoichiometric on palladium based catalysts. Thus, model reactions were studied. In lean burn conditions, methane oxidation by oxygen is favored whereas in rich conditions, the reduction of NO by methane becomes predominant. The authors showed also that the presence of CO inhibits the methane conversion in lean burn conditions. Furthermore, it is well known that the activity of noble metal catalysts depends on the O_2/CH_4 ratio. In presence of a large excess of oxygen, PdO seems to be most active phase for methane abatement [54]. Palladium based catalysts seem to be more active than platinum based ones.

In presence of oxygen, Pt and Pd are in PtO_2 and PdO form, respectively. PdO is formed between 300 and 400 °C, and is stable up to 800 °C. On the contrary, PtO_2 is metastable. It decomposes below 400 °C. Thus, in oxidizing mixture, the PdO and Pt^0 are the active phases, respectively [56]. The stability of the PdO phase depends on the support. Farrauto et al. [55] have shown that the PdO/Al_2O_3 decompose in air at around 850 °C whereas PdO/ZrO_2 decomposes 100 °C below. We have shown by characterizations that palladium was supported on alumina on the commercial catalyst. For methane oxydation by NO, Burch and Ramli [56] have compared Pd, Pt and Rh catalysts. The Pd-based catalysts is the most active in lean burn conditions. Under rich mixtures, they observed that Pt/Al_2O_3 is the more efficient. Recently, Da Costa et al. [5,6] have studied various commercial NGV converters in monolithic form under reaction mixtures close to the exhaust gases. Different authors have studied the kinetics of CH_4/O_2 reaction. In lean burn or in stoichiometric conditions, they found order 1 versus methane and 0 versus oxygen on alumina palladium or platinum supported catalysts [57,58].

3.2.3. Other TWC process reactions

Both steam reforming and water-gas shift are known to be promoted by three-way catalysts [5–14,16,17]. The relative importance of oxidation, steam reforming and water-gas shift over different catalysts have been the subject of some studies [10,18,11].

Other reactions can be involved in the TWC process such as:

(i) water-gas shift reaction

$$CO + H_2O = CO_2 + H_2 \tag{1}$$

(ii) methane steam reforming

$$CH_4 + H_2O = CO + 3H_2 \tag{2}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{3}$$

Whittington et al. [18] have already shown the importance of these reactions in TWC classical process. They compared the activity of a monolithic three-way catalyst with the performance of the individual metals (Pt, Pd, Rh) for steam reforming and water-gas shift. The presence of ceria was found to accelerate the last two reactions [16]. The orders of activity were found to be for steam reforming in absence of ceria, Pd > Rh > Pt; and in presence of ceria, three-way ~Rh > Pd > Pt; and for water-gas shift in absence of ceria, Pd > Pt > Rh; in presence of ceria, three-way > Pt > Pd > Rh. Both the water-gas shift and the steam reforming reactions became significant only at higher temperatures than those needed to facilitate oxidation. They also proposed that both reactions are probably important only after oxygen has been exhausted in the monolithic bed.

3.3. Effect of the concentrations on the catalytic performance of the commercial catalyst

Prior catalytic experiments, gas phase experiments were carried out, in order to point out the reactions involved in metallic reactor. No reaction is observed prior 450 °C. The CO is oxidized by metallic reactor at temperatures higher than 450 °C (maximum of 10% conversion at 500 °C). Then, only cordierite (1.9 in. × 1 in.) was used in the reactor. The conversion of CO begins around 300 °C and methane conversion is observed at $T > 425$ °C. But only 25% of methane and 30% of CO were converted at 500 °C.

Moreover, we carried out experiments in absence and in presence of CO_2. No significant changes were observed, thus we decided to work close to exhaust gases conditions, always using CO_2 in the feed.

In order to investigate the effect of the concentration of the exhaust gases, we considered two experimental conditions listed in Table 3, composition (A) and (B). The composition (A) is close to the composition representative to light vehicles filed by compressed natural gas [5], whereas the composition (B) is representative to heavy vehicles. For these two compositions are close to the stoichiometry (richness = 1.005, λ = 0.995).

In order to compare all the operating conditions, we plotted the conversion of three pollutants NO, CO and CH_4. The results are presented in Fig. 4a and b.

Let us focus first on NO conversion. The NO conversion follow a particular trend. Indeed, for both compositions, the NO conversion decreases with the temperature, then increases up to 100% at around 330 °C in light vehicles composition and 360 °C under heavy-duty composition.

At 100 °C, about 55% of NO is converted on both compositions. However, at this low temperature, the only product of the reaction is N_2O (Fig. 4a). However, at 100 °C, 300 ppm of NO are missing. This NO could be adsorbed and stored on the catalyst surface, because of the OSC such as barium oxi-carbonate or ceria present on the commercial material. The OSC was difficult to evaluate on this catalyst due to PdO phase, however, the support of the catalyst presents an OSC typical of Ce/Zr = 0.5, even the presence of Ba and La.

Furthermore, the N_2O selectivity decreases with the temperature. Only, after 200 °C, N_2 starts to be formed, at low temperature, less than 5% of N_2 is formed which corresponds to experimental error. This behaviour can be explained by a change of reducing agent with the temperature. According to the literature, at low temperature, the NO can be reduced by hydrogen or carbon monoxide [6–13,59,60,61]. At higher temperature, the methane is the reducing agent [28,62].

The N_2 formation coincides with the methane oxidation by NO. Thus, we can conclude that on the commercial catalyst the NO is only reduced in to N_2O at low temperatures (<200 °C), when the reducing agents are the hydrogen and the carbon monoxide. To verify this point, the effects of hydrogen and carbon monoxide have been studied on the commercial catalyst. The results are presented below.

We followed also the CO conversion. The catalyst is also active for CO oxidation at 100 °C, almost 85% of CO are oxidized. This result is in agreement with the literature [5–7,9–14]. The CO conversion is almost stable from 100 to 150 °C. Then, we can also notice a change in the slope of the plots of CO conversion (Fig. 4a and b) up to 150 °C. In our condition, we can propose that the CO is almost oxidized by the oxygen present in the feed. Thus at the same time, no more CO is available to reduced NO, NO is thus only reduced by hydrogen. To confirm this result, we removed the CO in the feed, in keeping the same richness (A/F ratio). The results are presented below.
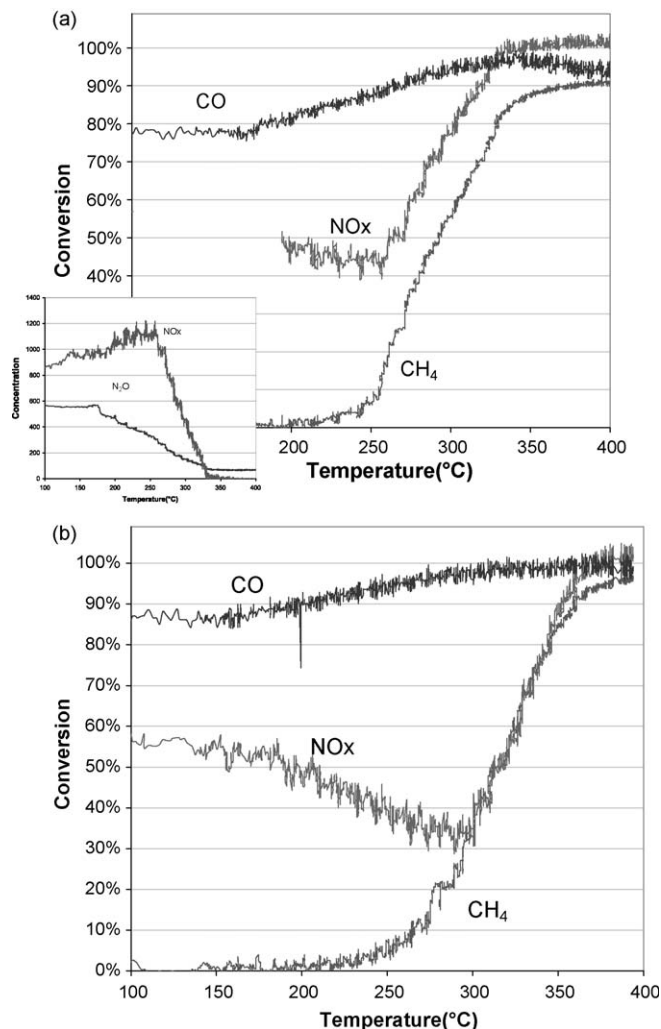
Fig. 4. Activity of car exhaust catalysts in terms of conversion of carbon monoxide, of nitrogen oxide and methane in complete feed gas as function of temperature. Following of concentration N_2O produced. (a) Feed gas: 2500 ppm NO, 3400 ppm H_2, 4700 ppm CO, 1700 ppm CH_4, 9.25% CO_2, 4800 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition A). (b) Feed gas: 1640 ppm NO, 2400 ppm H_2, 3300 ppm CO, 1230 ppm CH_4, 9.43% CO_2, 4100 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition B).

Finally, we focused also on the methane conversion. The TWC natural gas converter is composed mainly by palladium, and more particularly by PdO, which is known to be an active phase for methane oxidation [24,56]. For both compositions, the methane conversion follows the same trend. The methane conversion begins at ca. 220 °C. The light off temperature was found at ca. 277 °C for light vehicles conditions and around 320 °C for heavy-duty applications. Due to the concentration of oxygen in the feed, we can suppose that the methane is not only oxydized by molecular oxygen coming from O_2. Indeed, NO and water can be involved in methane oxidation [10,18,28].

XPS and TEM were performed after these two catalytic tests, and no significant change is obtained in Pd or Rh oxidation state and on size of particles.

3.4. On the effect of NO concentration on the catalytic performance of natural gas three-way catalysts (NG TWC)

In order to investigate the role of each gas on the catalytic performance of NG TWC, we began to study the effect of the NO

Table 4
Reaction temperature for the different NO concentrations.

NO_x concentration (ppm)	1500	2000	2500
T initial CH_4	236	233	237
T 50% CO	<100	<100	<100
T 50% CH_4	277	277	277

concentration. To compare all the data, the A/F ratio was always chosen to be equal to 0.995. Thus, we decreased the NO concentration from 2500 to 1500 in decreasing only the methane concentration (Table 3). The results are presented in Table 4 and Fig. 5. From that results, we can conclude that there is no significant differences in changing both NO and methane concentrations.

Indeed, the trends of the plots of NO reduction are similar. However, the degree of reduction at low temperature depends on the NO concentration.
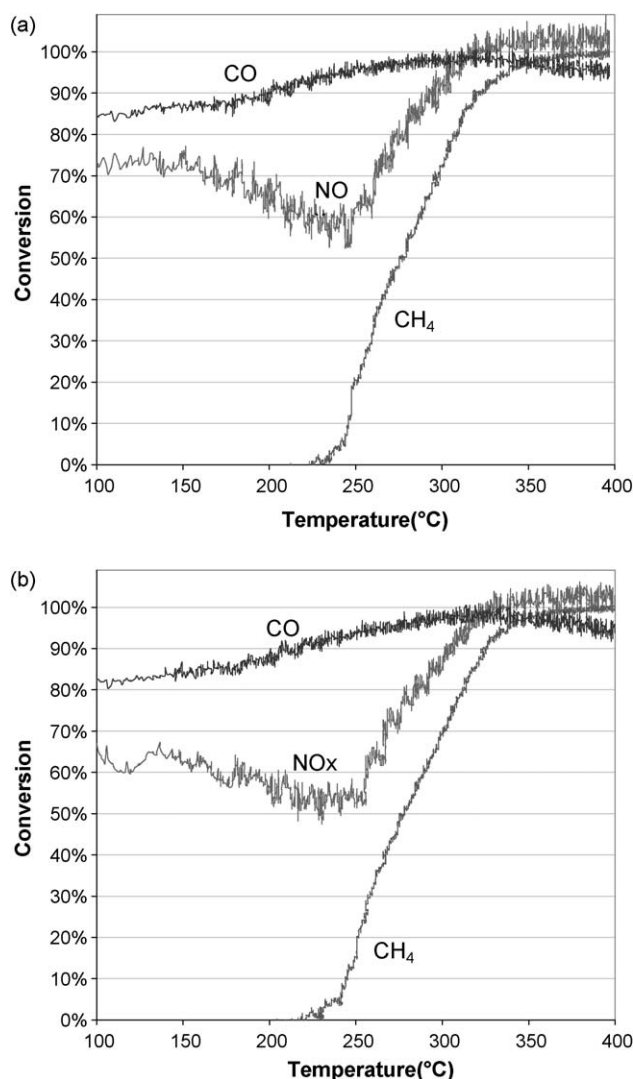
Fig. 5. Activity of car exhaust catalysts in terms of conversion of carbon monoxide, of nitrogen oxide and methane in complete feed gas as function of temperature. Following of concentration N_2O produced. (a) Feed gas: 1500 ppm NO, 3400 ppm H_2, 4700 ppm CO, 1400 ppm CH_4, 9.25% CO_2, 4800 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition C). (b) Feed gas: 2000 ppm NO, 2400 ppm H_2, 3300 ppm CO, 1550 ppm CH_4, 9.43% CO_2, 4100 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition D).

Table 5
Exhaust gases composition during the runs on the NGV converter, effect of reducer concentration.

	Composition E	Composition F	Composition G	Composition H	Composition I
NO (ppm)	2500	2500	2500	2500	2500
CH_4 (ppm)	0	500	1700	1700	1700
O_2 (ppm)	1500	0	2400	3000	4800
CO (ppm)	4700	2200	0	4700	4700
H_2 (ppm)	3400	1500	3400	0	3400
CO_2 (%)	9.25	9.25	9.25	9.25	9.25
H_2O (%)	18	18	18	18	0

For low NO concentrations (composition C) presented Fig. 5a, one can see that around 70% of NO is reduced at 100 °C, whereas for a feed containing 2000 ppm of NO, around 60% of NO is reduced at 100 °C (Fig. 5b). Finally, we have found previously ca. 50% for 2500 ppm of NO in the feed. These results are not surprising. Indeed, the concentration in reducing agent did not change, however, with a higher concentration of NO, the rates of NO adsorption and dissociation can be lower due to competitions with all the gases from the feed. These results can be correlated with the CO conversion. Indeed, the CO conversion increases at low temperature with the decrease of NO concentration (Figs. 4a and 5a and b).

At high temperature, the change of the NO concentration is minimized because of the change of methane concentration (Table 3). The same light-off temperatures were found for methane. This latter result leads us to conclude that the methane is the major reducing agent of NO for temperatures higher than 200 °C.

3.5. On the effect of reducing agents on NO abatement

3.5.1. Effect of hydrogen on NO abatement

The carbon monoxide and hydrogen are well known to be the reducing agents [59,60] of NO in TWC process. In order to investigate the role of each gas, hydrogen was first removed from the feed and the concentration of oxygen was decreased in order to keep the same richness (composition H, Table 5). The results were thus compared to those obtained in presence of hydrogen. In Fig. 6, one can see that the NO conversion decreases significantly in comparison to the overall mixture presented in Fig. 3. There is almost 10% NO converted at 250 °C in comparison to around 50% under global reaction mixture. The light off temperature is then shift of about 100 °C to higher temperatures. Moreover, the total reduction of NO is also shifted to high temperatures. Furthermore, at low temperature, the concentration of N_2O is lower than those obtained with the global mixture, with about 50% of selectivity.

These results obtained in absence of hydrogen let us to conclude that the major reducing agent for NO reduction at low temperature is the hydrogen. At temperatures lower than 200 °C, the hydrogen reacts with the adsorbed oxygen atoms, leading to N_2O formation. However, at higher temperature, the hydrogen can be oxidized by the oxygen and then the reduction of NO by H_2 stops.

The CO present in the feed is only oxydized by oxygen. And thus, no CO would be available for the reduction of NO. Thus, we can also propose that the CO oxidation and NO reduction do not take place on the same active sites. We can propose that the CO oxidation takes place on Rh oxidized sites, because rhodium is dispersed on ceria zirconia [50]; and NO reduction takes place on palladium sites.

As the catalyst is a commercial three-way catalyst and is composed by Pd, Rh and a low amount of Pt. Studies are in course to explain that point with honeycomb catalysts containing only Pd, Pt or Rh. At higher temperatures, up to 200 °C, the methane becomes

the reducing agent. No significant changes are observed between Figs. 3 and 6.

The overall reaction is then:

$$CH_4 + 4NO = 2N_2 + CO_2 + 2H_2O \qquad (4)$$
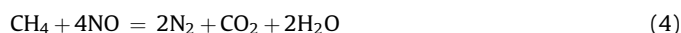
Due to the complexity of the gas mixture, the inhibiting process cannot be clearly identified. Indeed, the methane oxidation by
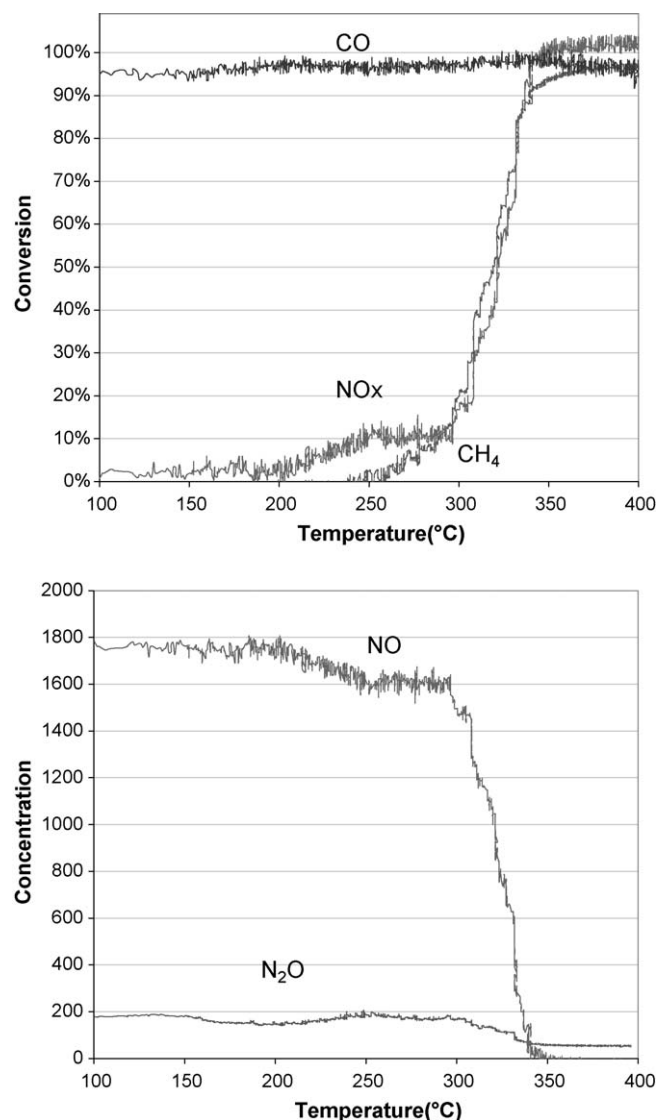
Fig. 6. Activity of car exhaust catalysts in terms of conversion of carbon monoxide, of nitrogen oxide and methane in absence of hydrogen in feed gas as function of temperature. Concentration N_2O produced. Feed gas: 2500 ppm NO, 0 ppm H_2, 4700 ppm CO, 1700 ppm CH_4, 9.25% CO_2, 3000 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition H).
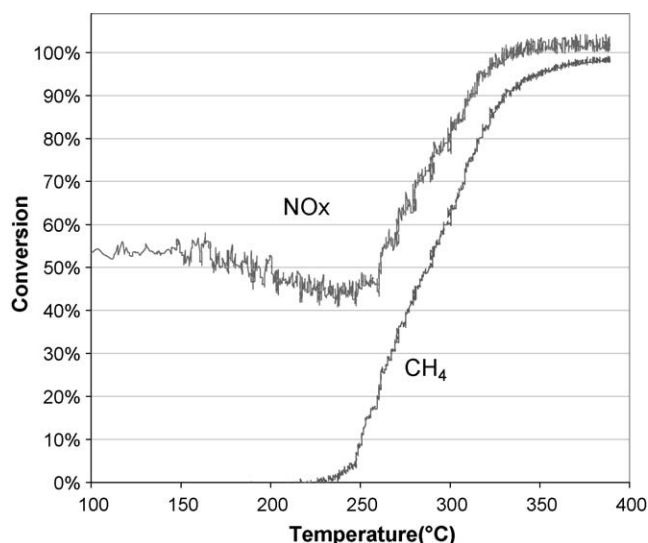
Fig. 7. Activity of car exhaust catalysts in terms of conversion of nitrogen oxide and methane in absence of CO in feed gas as function of temperature. Feed gas: 2500 ppm NO, 3400 ppm H_2, 0 ppm CO, 1700 ppm CH_4, 9.25% CO_2, 2400 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition G).

Table 6
Reaction temperature for the composition A and G.

	With CO	Without CO
T end NO_x	315	330
T initial CH_4	237	240
T 50% CH_4	277	290

oxygen is in competition with the reduction of NO. To verify that point one experiment was performed in absence of oxygen. The results are presented below.

As conclusion, at low temperature, the NO is mainly reduced by hydrogen. At higher temperature, the methane plays the role of reducer. Finally, this reaction is possible because in the overall gas mixture the ratio H_2/CO is 0.7 which is higher than a typical TWC process for gasoline applications and because the methane is the major hydrocarbon unburned from natural gas vehicles.

3.5.2. Effect of CO on NO_x abatement

From Fig. 3, we can note that more than 60% of CO is converted in CO_2 below 100 °C. As we proposed, the main reaction is the CO oxidation by O_2. In the literature, Authors argue that the reaction CO/NO does not take place since there is still adsorbed oxygen or an excess of oxygen in the feed [50]. In our experimental conditions (composition A), we could estimate the amount of oxygen left. From CO + 1/2O_2 = CO_2, an excess of 4900 ppm of oxygen (O) is found. From H_2 + 1/2O_2 = H_2O, about 1500 ppm of oxygen in excess was found.

In order to confirm that the major reducing agent is the hydrogen, the carbon monoxide was removed from the feed (Table 5). The results are presented in Fig. 7. In absence of CO, the global trends of the plots of NO reduction and methane oxidation are similar. Even if CO is well known to be a reducing agent in typical TWC process, for our application and in presence of the commercial catalyst, the CO does not reacts with NO. We can propose that the CO oxidation and the NO reduction do not take place on the same site. Furthermore, as less N_2O is detected, we can also suppose a reaction between CO and N_2O, product of NO decomposition or reduction at low temperature. The reaction being:

$$CO + N_2O = N_2 + CO_2 \qquad (5)$$

McCabe and Wong have studied the partial order in CO and N_2O between 564 and 583 K. The results have shown a negative order in CO which represents a competitive adsorption between N_2O and CO, and a favored CO adsorption [61]. The reaction could take place below 100 °C. Indeed, more that 80% of CO is converted and a large

amount of N_2O is detected, however, more investigations in simplest conditions have to be done.

Finally, from Table 6 and Fig. 7, one can note that no changes are observed at low temperatures, as already discussed above. However, the reaction temperatures change at high temperature, indicating that CO is involved on other reactions. Whittington et al. have studied oxidation and water-gas shift reactions [18]. They proposed, using simulated exhaust gas, that oxidation was found to occur at lower temperatures than either of the other reactions, suggesting that reactions involving steam become significant only when oxygen is absent or when the catalyst temperature is higher. If at high temperatures, the water-gas shift reaction occurs, in presence of CO (Fig. 3), the reaction leads to H_2 which is a potential reducing agent. Then, all the process of TW is enhanced. Thus the reaction temperatures should be shifted to lower temperatures. In Table 6, we can see that in presence of CO the $T_{100\%}$ of NO reduction is shifted to 15 °C to low temperature.

We investigated the effect of water on the activity of CNG, the results are discussed below.

3.5.3. Effect of methane on NO abatement

From Fig. 3, one can see that methane is converted for temperatures higher than 220 °C. This activation temperature is representative of palladium [24,28,56]. The active site for methane oxidation is mainly the palladium which was found as palladium in +II oxidation state before and after runs. As, the major noble metal on the commercial catalyst is palladium, we assume that the reaction takes place on that site.

The methane conversion increases with the temperature. The plots of methane conversion and NO conversion have the same slopes. We propose that at high temperature the NO is reduced by CH_4. These results are in agreement with those presented in the
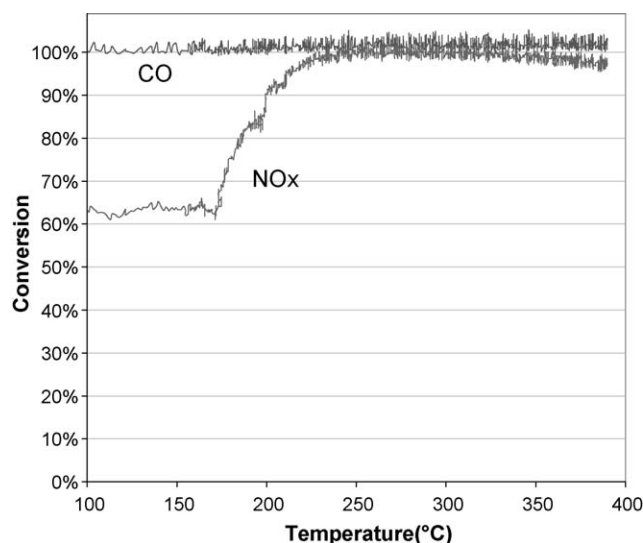
Fig. 8. Activity of car exhaust catalysts in terms of conversion of carbon monoxide and nitrogen oxide in absence of CH_4 in feed gas as function of temperature. Feed gas: 2500 ppm NO, 3400 ppm H_2, 4700 ppm CO, 0 ppm CH_4, 9.25% CO_2, 1500 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition E).
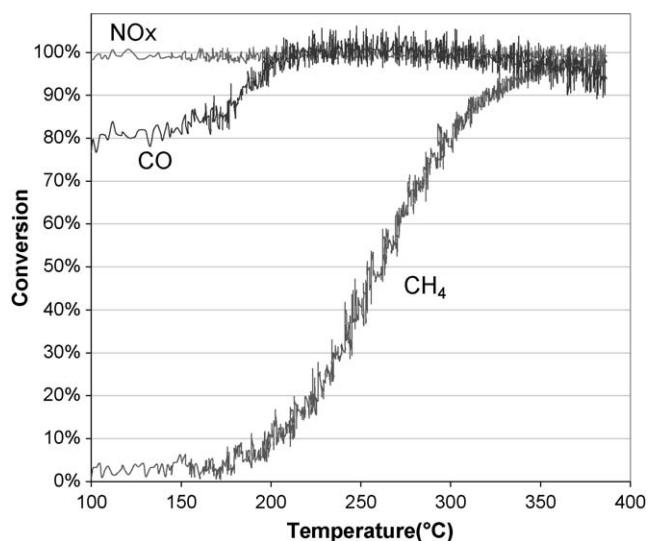
Fig. 9. Activity of car exhaust catalysts in terms of conversion of carbon monoxide, of nitrogen oxide and methane in absence of oxygen in feed gas as function of temperature. Feed gas: 2500 ppm NO, 1500 ppm H_2, 2200 ppm CO, 500 ppm CH_4, 9.25% CO_2, 0 ppm O_2, 18% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition F).

literature [28,56]. In removing the methane of the feed, we notice that the NO totally reduced at low temperature (Fig. 8). This result was expected because there is less oxygen in the feed, thus, the NO reduction is favored. In these experimental conditions, the oxygen concentration is only 0.18% vs. 0.45% in overall mixture.

3.6. Other important reaction involved

3.6.1. Effect of oxygen

We investigate the effect of oxygen, in removing it from the feed. The results are presented in Fig. 9 and Table 7. At 100 °C, almost 80% of CO is oxidized. These results are similar to those obtained in presence of oxygen. This point can be explained by the oxygen storage capacity materials present on the catalyst. Indeed, ceria and barium oxides are present on the surface of the catalyst. At higher temperature, the conversion is 100%. Such high conversion can be explained by WGS reaction already described in the literature [18].

At low temperature, as no oxygen is present in the feed. 100% of NO is reduced by hydrogen or by CO [59,60], in these conditions (absence of oxygen in the feed) we cannot avoid the CO/NO reaction as proposed in TWC NGV conditions. NO decomposition can also occur on these conditions [62]. At higher temperature, the hydrogen does not react with O_2 and then is always present as reducing agent for NO abatement. At higher temperature, methane can also be a reducing agent. As there is no competition between oxygen and NO, we note that the light off temperature of methane is shifted to lower temperature. Thus, NO/H_2 and NO/CH_4 reactions could take place. Marques et al. [28] have shown that the methane reduces NO in absence of oxygen. In that case, a reduction of "PdO" active phase is observed. XPS analyses have shown that a part of

palladium (20% of total palladium) is reduced in these operating conditions. A second run was carried out in order to check the activity of the reduced catalyst. Then, a slight increase in light of temperature of methane oxidation is observed, leading to the conclusion that PdO or Pd^{2+} are mainly the active phases for TWC process, even if a REDOX process cannot be excluded due to the oscillations of richness.

3.6.2. Effect of water

Two overall reactions can occur during TWC process: water-gas shift and steam reforming of methane.

3.6.2.1. Water-gas shift reaction. In presence of total gas mixture (Fig. 3), we note a decrease of CO conversion at high temperature. This decrease could be explained the water-gas shift reaction. In the feed, about 18 wt.% of water is present which is representative of the exhaust concentration of CNG vehicles. Whittington et al. [18] have already shown the importance of these reactions in TWC classical process using feed representative of exhaust gases from gasoline engines. To verify that the WGS reaction takes place in the
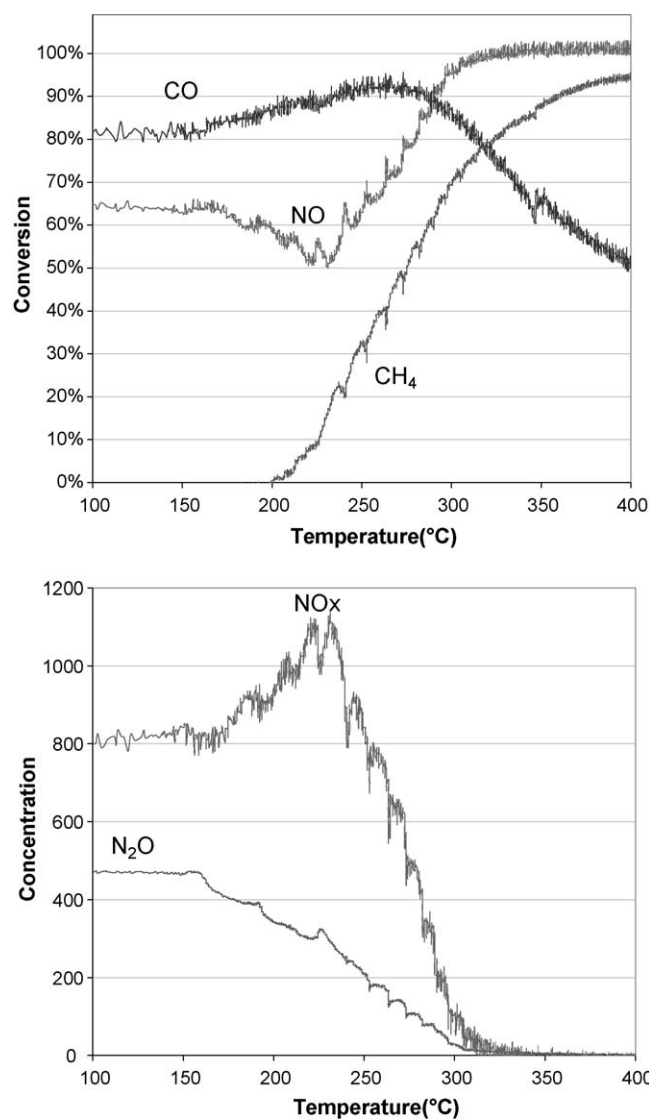
Fig. 10. Activity of car exhaust catalysts in terms of conversion of carbon monoxide, of nitrogen oxide and methane in dry feed gas as function of temperature. Feed gas: 2500 ppm NO, 1500 ppm H_2, 2200 ppm CO, 500 ppm CH_4, 9.25% CO_2, 0 ppm O_2, 0% H_2O and balance N_2 at GHSV 40,000 h^{-1} (composition F).

Table 7
Reaction temperature for the composition A and F.

	With O_2	Without O_2
T end CO	300	200
T end NO$_x$	<100	<100
T initial CH_4	243	180
T 50% CH4	277	250

course of the global reaction, the water was removed from the feed. Then, we followed the conversion of the major pollutants (Fig. 10).

At low temperature, the water presence does not affect the CO oxidation reaction. About 80% CO is converted in presence or in absence of water (Figs. 3 and 10). At low temperature, the water only plays a role of ligand and occupies the actives sites, and thus inhibits some reactions. Thus, NO reduction is affected by the presence of water. About 10% less conversion was obtained in presence of water up to 200 °C. At higher temperature, neither significant changes are observed on CO nor NO conversion plots.

Furthermore, we note in the plots a decrease of CO conversion only at high temperature. From 250 °C, the CO conversion decreased and is only ca. 50% at 400 °C. The same amount of oxygen is present in absence of water, if a decrease is observed on CO abatement in absence of water this implies that the CO transformation takes places through another reaction: the WGS reaction.

These results are in agreement with those presented by Willington et al. [18] and those in the review of Barbier and Duprez [10,16].

3.6.2.2. Steam reforming of methane.

At high temperature, after the total NO conversion, the methane is still oxidized. This oxidation cannot be only due to the oxidation with oxygen or with the NO, because of the composition (rich conditions). The runs realized in absence of water (Fig. 9) are compared to those realized in presence of water.

Two phenomena are identified. Again, first, at low temperature (below 250 °C), the water presents an inhibitor effect on the methane conversion. The water plays the role of ligand on the sites of methane oxidation and thus inhibits the reaction. Moreover, the water can lead to a deactivation by modifying the palladium species in the course of the reaction. Thus, the water adsorbs on palladium (Pd^{2+}) surrounded by oxygen or PdO and $Pd(OH)_2$ are then formed. It is well known that these species are less active for methane oxidation [61].

From 260 °C, the reverse phenomenon is observed. The methane conversion decreases in absence of water. This later results leads to the conclusion that water is involved on methane abatement at high temperature (Eqs. (2) and (3)).

4. Conclusions

The commercial honeycomb converter is mainly composed by palladium oxide «PdO», about 2.55 wt. %. A small amount of rhodium (0.18 wt.%) is also present at the surface of catalyst, and only 0.07 wt.% of platinum is detected. By STEM, we could conclude that the palladium is deposed on alumina whereas rhodium is deposed on ceria–zirconia. No platinum was found at the surface by XPS, whereas a BaO phase was evidenced.

This commercial catalyst was tested in a synthetic gas mixture representative of exhaust gases from CNG vehicles. The GHSV was chosen equal to 40,000 h^{-1} and the richness was 1.005. In order to attribute a role of each gas present in the real exhaust gases, we decided to study systematically the role of each one in removing it from the feed in keeping the same richness to compare all the presented results.

From this study, one can conclude that two temperature reaction domains can be identified: from 100 to 250 °C involving coupled CO/O_2 and NO/H_2 reactions and from 250 to 400 °C involving coupled CO/H_2O and CH_4/O_2 CH_4/NO CH_4/H_2O reactions.

At low temperature, the CO is only oxidized by oxygen. Simultaneously, the NO is only reduced by the hydrogen present in the feed (H_2/CO = 0.7). Only N_2O is produced.

The CO_2 does not have any effect of the reaction, whereas the water inhibits the reactions at low temperatures. As the catalyst is complex, we can propose that all the reactions involved in TWC process do not take place on the same sites. Investigations are in course in using a commercial catalyst containing only palladium.

At higher temperature, the methane is activated and oxidized into CO_2. The main oxidizing agent of methane is NO. However, at high temperature, the steam effects are not negligible. Thus, in absence of water, the CO and methane are not 100% converted at medium temperature. Water-gas shift and Methane steam reforming take part in TWC process in CNG conditions as well for gasoline [10].

Thus, in CNG stoechiometric applications, at low temperatures CO/O_2, NO/H_2 are identified. Never, the NO is reduced by CO.

At high temperature, CO/O_2, NO/H_2 are completed by CH_4/O_2, CH_4/NO, H_2/O_2, and CO/H_2O, CH_4/H_2O. The presence of steam (18 vol.%) affects the global activity of CNG converters.

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